I. PREPARATION AND RESOLUTION OF PROPERLY SUBSTITUTED ARYL ACRYLIC ACIDS

II. STUDIES IN LARGE RING FORMATION

BY

JOHN WALTER MECORNEY

B. S., University of California, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE
UNIVERSITY OF ILLINOIS, 1944

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I. PREPARATION AND RESOLUTION OF PROPERLY SUBSTITUTED ARYL ACRYLIC ACIDS

Introduction

The preparation and resolution of properly substituted aryl acrylic acids has been under investigation by Adams and his coworkers[1]. Of some twenty-five of these acids which have been reported, the twelve that have been resolved all contain bromine or chlorine atoms in the β-position. The present investigation was designed to introduce the methyl group in the β-position and to compare the effective radius of the methyl group with that of the chlorine atom by determinations of the half life values.

Discussion

Adams and Gross[2] were able to prepare and resolve α-methyl-β-chloro-β-(2,4-dimethyl-3-chloro-6-methoxyphenyl)-acrylic acid (I.) They found that the half life of this substance at 44° in *n*-butyl alcohol was 173 minutes. They were also able to resolve β-chloro-β-(2,4-dimethyl-3-chloro-6-methoxyphenyl)-acrylic acid (II), which had a half life of nine minutes under the same conditions.

α,β-Dimethyl-β-(2,4-dimethyl-6-methoxyphenyl)-acrylic acid (III) was prepared and resolved. The half life at 44° in *n*-butyl alcohol was found to be 73.8 minutes. At 22° with the same solvent it was found to be 700 minutes. Comparison with I shows that the methyl group is only 40% as effective as the chloro in this series. β-Methyl-β-(2,4-dimethyl-3-chloro-6-methoxyphenyl)-acrylic acid (IV.) was prepared but could not be resolved and comparison with II was not possible.

The following acids were prepared but whose resolution could not be effected: β-methyl-β-(2,4-dimethyl-3-nitro-6-methoxyphenyl)-acrylic acid, β-methyl-β-(2,4-dimethyl-6-methoxyphenyl)-acrylic acid, β-methyl-β-(2,4-dimethyl-6-methoxyphenyl-*N*-acrylyl glycine, α,β-dimethyl-β-(2,4-dimethyl-3-nitro-6-methoxyphenyl)-acrylic acid and α,β-dimethyl-β-(2,4-dimethyl-3-chloro-

6-methoxyphenyl)-acrylic acid. Evidence is given for the *cis*-configuration of all these aryl acrylic acids.

It has been reported[3] that the von Pechmann condensation of ethyl acetoacetate and phenols leads invariably to coumarins. It was found that 4-chloro-3,5-dimethylphenol when condensed with ethyl acetoacetate in the presence of concentrated sulfuric acid, led to 6-chloro-2,5,7-trimethylchromone instead of the expected coumarin[4]. The structure of the chromone was established by formation of a styryl derivative, by various hydrolytic reactions and by an unequivocal synthesis. It was thus demonstrated that the von Pechmann condensation does not always yield coumarins as previously reported.

II. STUDIES IN LARGE RING FORMATION.

Introduction

Adams and Kornblum[5] were able to prepare and resolve 2,2′-dicarboxy-5,5′-(decamethylenedioxy)-biphenyl and its octamethylene homolog. This research was concerned with a new route to this type of molecule and to attempt to extend the direct condensation of two *w,w′*-bifunctional molecules[6].

Discussion

In the preparation of 2,2′-dicarboxy-5,5′-(decamethylenedioxy)-biphenyl. Adams and Kornblum found that the last step involving the oxidation of the 2,2′-dimethyl groups to the dicarboxybiphenyl was attended with unusual difficulties.

A new synthesis was devised in which 2,2′-dimethyl-5,5′-dimethoxybiphenyl was oxidized to 2,2′-dicarboxy-5,5′-dimethoxybiphenyl (I.) All attempts to demethylate I to 2,2′-dicarboxy-5,5′-dihydroxybiphenyl were unsuccessful, however. These methods included the use of mineral acids, aluminum chloride, pyridine and aniline hydrochlorides and concentrated alkali. The dibasic acid was converted to the imide and the diamide. These two compounds also failed to possess the desired properties toward demethylating agents.

2,2′-Dimethyl-5,5′-(heptamethylenedioxy)-biphenyl has been prepared by using the high dilution apparatus of Adams and Kornblum[5] in the course of 354 hours from 2,2′-dimethyl-5-hydroxy-5′-(*w*-bromo-*n*-heptyloxy)-biphenyl in 22% yield.

Bibliography

1 Adams and Theobald, J. Am. Chem. Soc., **65**, 2383 (1943).

2 Adams and Gross, ibid., **64**, 1786 (1942).

3 Chakravarti, J. Ind. Chem. Soc., **12**, 536 (1935).

4 Adams and Mecorney, J. Am. Chem. Soc., **66**, 802 (1944).

5 Adams and Kornblum, ibid., **63**, 188 (1941).

6 Adams and Whitehill, ibid., **63**, 2073 (1941).

Vita

The writer was born in Bakersfield, California, on April 17, 1918. He received his elementary education in the public schools of Bakersfield and Berkeley, California. He was graduated from Berkeley High School in January, 1936. In August, 1936, he entered the University of California where he studied until May, 1938, and from August, 1939, to September, 1941, when he received the degree of Bachelor of Science. In the fall of 1941 he enrolled in the graduate school of the University of Illinois, where he held the position of teaching assistant during the academic years 1941-2, 1942-3 and 1943-4.

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